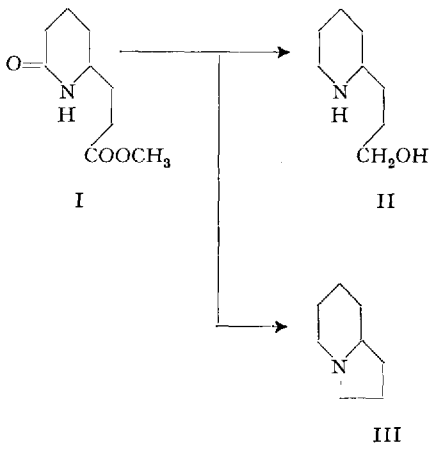
succinic acid[2], has been described, with the statement that the reaction does not appear to be of general application. Realizing the possible use of this new method, especially in the synthesis of alkaloids, we



started some preliminary work on this subject. Our results are summarized in the following Table, from which it appears that secondary amines, with the nitrogen atom belonging to a ring system, as well as lactames are alkylated by carboxylic acid esters in the presence of $LiAlH_4$.

N-component	Ester component	Product obtained	Yield %
2-Piperidone	Ethylacetate	N-Ethyl-piperidine	34
2-Piperidone	Benzylbenzoate	N-Benzyl-piperidine	20
Pyrrolidine	Ethylacetate	N-Ethyl-pyrrolidine	22
Piperidine	Ethylacetate	N-Ethyl-piperidine	29
Piperidine	Benzylbenzoate	N-Benzyl-piperidine	48

However, the N-alkylation of a monosubstituted amide under similar conditions has also been observed recently[3]. Using ketones and aldehydes as potential alkyl groups no alkylation product could be isolated.

Further work is in progress with the goal of increasing yields and determining the width of application of this reaction. Experimental details will be published elsewhere.

A. SEGRE and R. VITERBO

Research Laboratories of Farmochimica Cutolo-Calosi S.p.A., Napoli (Italy), October 10, 1957.

Riassunto

Viene descritto l'uso dell'idruro di litio e alluminio quale agente alchilante-riduttore nella reazione di lattami od ammine secondarie, con atomo di azoto appartenente ad un anello, con esteri di acidi carbossilici, per ottenere ammine terziarie.

[2] V. C. BARRY and D. TWOMEY, Abstracts of papers, *XIIth International Congress of Pure and Applied Chemistry* (New York 1951), p. 308.

[3] We thank kindly Dr. J. KALVODA, Laboratorium für organische Chemie, Eidgenössische Technische Hochschule, Zürich, for this communication.

Surface Exchange Adsorption between Precipitates of $BaSO_4$ and Solutions of $BaCl_2$, $Pb(NO_3)$, $CaCl_2$, CsCl, NaCl, and Na_2CrO_4

Some time ago we described[1] the preparation of precipitates of $BaSO_4$ and the determination of their specific surface area by means of surface exchange adsorption with a saturated solution of radioactive Ba^*SO_4.

We have now studied the exchange adsorption of these precipitates with solutions of radioactive Ba^*Cl_2, $Pb^*(NO_3)_2$, Ca^*Cl_2, Cs^*Cl, Na^*Cl, and $Na_2Cr^*O_4$. The radioactive isotopes used were:

Isotope	$\tau_{1/2}$	Specific Activity	Rays
Ba 131	13·0 d	1 mc/g	EC, γ
Pb 210	25 y	50 mc/g	β, γ
Ca 45	164 d	1 mc/g	β
Cr 51	27·8 d	2 mc/g	EC, γ
Na 22	2·6 y	Carrier free	β^+, γ
Cs 134	2·3 y	0·75 mc/g	β^-, γ

Suitable volumes (ranging from 1–10 cm^3) of solutions of radioactive salts of suitable initial concentrations (ranging from

2×10^{-2} to 2×10^{-5} eq./l of $BaCl_2$
5×10^{-3} to 3×10^{-4} eq./l of $Pb(NO_3)_2$
1×10^{-3} to $2{\cdot}3 \times 10^{-5}$ eq./l of $CaCl_2$
5×10^{-3} to 5×10^{-7} eq./l of NaCl, and CsCl
1×10^{-3} to 2×10^{-6} eq./l of Na_2CrO_4)

were shaken for 10, 20, 30, and 40 min in *p v c* tubes with suitable amounts of precipitate of $BaSO_4$ (ranging from 25–1000 mg),. then centrifugated and counted; the results were plotted as a function of the time of adsorption and extrapolated to $t = 0$ in order to obtain the exchange with the surface layer only.

The results were interpreted by means of the well-known equation for surface exchange adsorption equilibrium[2], stating that the ratio of the total numbers of Ba-ions in the solution and in the surface of the precipitate, and the corresponding number for Pb-ions are in a constant proportion, f(Pb). For the special case of a Ba-salt in solution, $f(Ba) = 1$. If the volume of the solution is v, the equilibrium concentration c, the mass of precipitate g, the number of equivalents exchanged per g of $BaSO_4$ x, the number of exchangeable cation equivalents per g of $BaSO_4$ t, we have the formula

$$\frac{gx/g\,(t-x)}{cv/gx} = f \quad \text{or} \quad \frac{gx}{cv} = -f + ft\,\frac{1}{x} \qquad (1).$$

Therefore we have plotted gx/cv as a function of $(1/x)$ (Fig. 1*a* for $BaCl_2$ and $Pb(NO_3)_2$; Fig. 1*b* for $CaCl_2$). Straight curves are obtained. The curve for $BaCl_2$ shows a value $f(Ba) = 1$, as required; $f(Pb) = 0{\cdot}44$; for $CaCl_2$ the straight line passes so nearly through the origin, that f(Ca) cannot be obtained from the Figure.

The lines for $Pb(NO_3)_2$ and $BaCl_2$ both yield a value for $t = 1{\cdot}4 \times 10^{-5}$ eq./g. If this value is known, the value f(Ca) can be obtained from the slope of the straight line in Figure 1*b*; this yields $f(Ca) = 0{\cdot}00137$.

We also studied the adsorption of NaCl, CsCl, and Na_2CrO_4 from aqueous solutions; there was no measur-

[1] A. J. RUTGERS and W. VAN DEN HEUVEL, Exper. *9*, 481 (1955).

[2] I. M. KOLTHOFF and W. M. MAC NEVIN, J. Amer. chem. Soc. *58*, 499 (1936).

able adsorption, or only a very slight one. For CsCl we also studied the adsorption from a mixture of 88·88% dioxane and 11·12% water (volume percentage). Conductivity measurements showed that CsCl was present here in undissociated form; the adsorption could be measured, and could be represented at low concentrations by a Langmuir isotherm, or by a Freundlich isotherm with $n = 0{\cdot}92$.

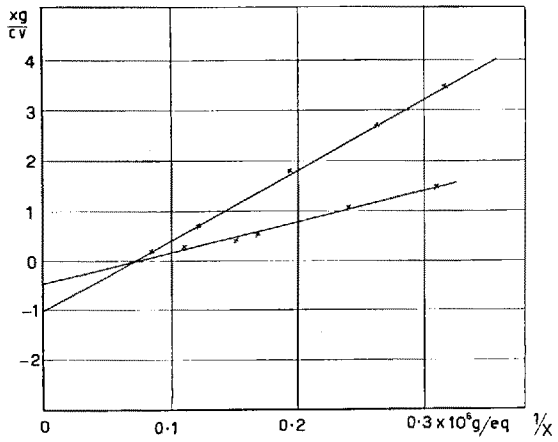


Fig. 1*a*. – gx/cv as $f(1/x)$ for solutions of $BaCl_2$ and $Pb(NO_3)_2$.

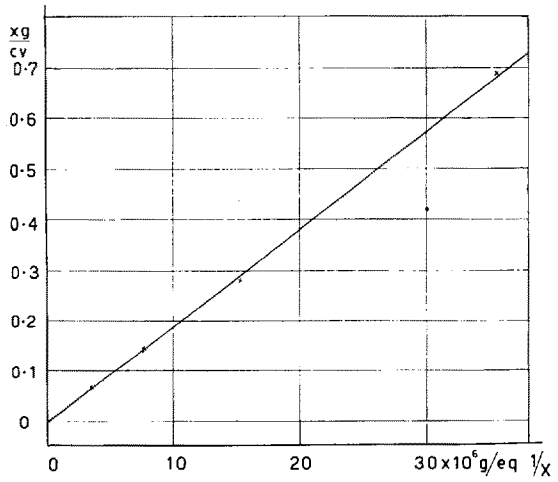


Fig. 1*b*. – gx/cv as $f(1/x)$ for solutions of $CaCl_2$.

The authors gladly express their gratitude to the Interuniversitair Instituut voor Kernwetenschappen and to l'Union Minière du Haut Katanga, who by their grants have enabled the authors to perform this research.

A. J. RUTGERS and W. VAN DEN HEUVEL

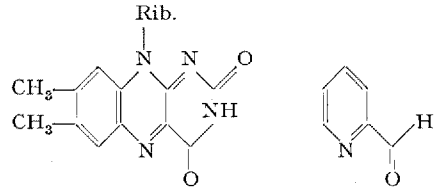
Laboratorium voor Physische Scheikunde der Rijksuniversiteit te Gent, September 26, 1957.

Résumé

Nous avons étudié l'adsorption d'échange entre des précipités de $BaSO_4$ et des solutions de $BaCl_2$, $Pb(NO_3)_2$ et $CaCl_2$ à l'aide de «tracers». Nous avons trouvé que l'adsorption peut être représentée par l'équation (1) pour l'adsorption d'échange; la capacité d'adsorption de notre $BaSO_4$ était égale à $1{,}4 \times 10^{-5}$ éq./g. Les grandeurs caractéristiques f, figurant dans l'équation pour l'adsorption d'échange, avaient les valeurs $f(Ba) = 1$; $f(Pb) = 0{,}44$; $f(Ca) = 0{,}00137$. Il n'était pas possible de démontrer l'adsorption de CsCl, NaCl or Na_2CrO_4 de solutions aqueuses.

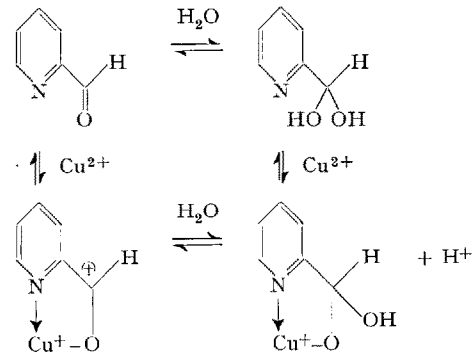
Metallchelate des Picolinaldehyds

Im Rahmen von Untersuchungen über die Chelatbildung von Riboflavin (I) und flavinähnlichen Modellsubstanzen konnten wir feststellen, dass Picolinaldehyd (II)



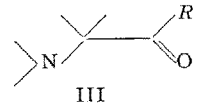
I II

bei der pH-Titration in Gegenwart von Cu^{2+} schon ab pH 4 Azido-Komplexbildung zeigt, obwohl der freie Ligand selbst über keinen beweglichen Wasserstoff verfügt. Die freigewordenen H^+ müssen demnach dem Milieu entstammen, und wir deuten diese «Pseudo-Azido»-Komplexbildung nach dem folgenden Schema:



Wir konnten ferner bei pH 7–8 einen sehr stabilen, kristallinen hellvioletten Festkörper isolieren, welcher keine Anionen enthält. Picolinaldehyd lässt sich daraus durch Ansäuern unverändert zurückgewinnen. Die Verbrennungsanalyse ergibt die Zusammensetzung $Cu \cdot (Aldehyd)_2 \cdot (OH)_2$. Auch der Festkörper lässt sich demnach vom stabilisierten Aldehyd-Hydrat ableiten.

Wir nehmen an, dass allgemein die CO-Funktion zweizähniger Liganden der Form III



III

durch Schwermetallion polarisiert wird, so dass die Anlagerung nukleophiler Partikel des Milieus (zum Beispiel H_2O, Alkohole, Amine) stark begünstigt ist. Bei Carboxyl-Gruppen wird so die Ausbildung stabiler «ortho»-Konfigurationen ermöglicht. Ein solcher Mechanismus wird von KLOTZ[1] für die metallkatalysierte Hydrolyse von Peptid-Bindungen vorgeschlagen. Die Ester der Picolinsäure zeigen bei der pH-Titration in Gegenwart von Cu^{2+} ein analoges Verhalten wie Picolinaldehyd. Es handelt sich hier offenbar um eine besondere Klasse von Komplexbildnern.

Über eine ausführliche Untersuchung der genannten Phänomene soll demnächst berichtet werden.

[1] I. M. KLOTZ, *Symposium on 'The mechanism of enzyme action'* (John Hopkin Press, Baltimore 1954), p. 280.